Author(s): Miettunen, Kati & Toivola, Minna & Hashmi, Ghufran & Salpakari, Jyri & Asghar, Imran & Lund, Peter

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A carbon gel catalyst layer for the roll-to-roll production of dye solar cells

Kati Miettunen[*]*, Minna Toivola, Ghufran Hashmi, Jyri Salpakari, Imran Asghar, Peter Lund*

New Energy Technologies Group,
Department of Applied Physics,
Aalto University[**],
P.O. BOX 15100, FIN-00076 Aalto, Finland

*Corresponding author. Fax: +358 9 451 3195. E-mail address: kati.miettunen@tkk.fi. (K. Miettunen)

[**] formerly Helsinki University of Technology

Abstract

Carbon gel catalyst layers were used in dye solar cells. These layers were prepared on flexible plastic substrates at low temperatures (130 °C). The carbon gel, demonstrated excellent flexibility which is an important feature for roll-to-roll production and special applications of dye solar cells. The use of these low cost and highly flexible catalyst layers resulted in good photovoltaic performance; only 10 % lower than dye solar cells with rigid glass-based counter electrodes prepared with thermal platinization at ~400 °C temperature.

1. Introduction

Nanostructured dye solar cells (DSC) [1] represent a potentially cheap photovoltaics option due to simple manufacturing methods and cheap materials. Traditionally DSC have been prepared on glass substrates equipped with transparent conducting oxide (TCO). Although glass is a good option in terms of performance and stability [2, 3], its high cost [4] and preparation limited to batch production motivate to find alternatives. A key issue in the commercialization of the DSC is to use roll-to-roll mass production methods to enable cost-effective solutions. Firstly, flexible substrates such as plastics are needed for roll-to-roll production. Secondly, flexibility of the electrode on top of the substrate is required. For instance Miyasaka et al. have demonstrated flexible photoelectrodes that give good cell efficiency (5.8 %) [5].

In this work the focus is on counter electrodes. The main task of a counter electrode is to efficiently return the charge from the counter electrode back to electrolyte. Low charge transfer resistances are reached with Pt catalyst layers which are commonly prepared with a high temperature treatment at ~400 °C [6]. To lower the cost, the use of carbon has been introduced [7]. The structures of DSC with Pt and porous carbon catalyst layers are show in Figure 1. To compensate the high charge transfer resistance of carbon, the carbon film is thick, usually around 10-20 μm, in order to have large surface area for the catalyst reaction [7]. To create good bonding between the particles which is needed to get high conductivity in the catalyst film, the layer is normally sintered is heat treated at high temperatures (~450 °C) [7].

When flexible plastic substrates are used, low temperature methods (<150 °C) are required. Instead of sintering, low temperature pressing has been employed to get good connection between the particles [8, 9]. These low temperature layers have provided low charge transfer resistance 0.5-2 Ωcm^2 [9]. There have, however, been problems with the flaking of the catalyst layer and the related

poor flexibility [9]. Good flexibility of the counter electrode catalyst layer is, however, essential for roll to roll mass production and also important for special applications.

In this work we gelatinize carbon paste and combined it to the previously developed pressing method to produce good adhesion between the particles and achieve sufficient flexibility for roll-to-roll production. The inspiration for this work came from our previous study, in which very thick carbon gel was used in a dye solar cell type photovoltaic fiber sensor [10]. In that application, the current was minimal, in the range of nA, [10] and the electrical performance of the carbon film were not sufficient to be used as such in normal DSC.

The photovoltaic performance of a DSC equipped with a carbon gel catalyst layer on conducting plastics is measured. The flexibility and the related mechanical stability are evaluated with bending tests. To analyze the electrochemical performance, in particular charge transfer resistance, also electrochemical impedance spectroscopy (EIS) measurements are made.

2. Experimental methods

The carbon gel paste was prepared as follows: 1.6 g of graphite powder (synthetic, conducting grade, -325 mesh, Alfa Aesar), 0.4 g of carbon black (Printex XE2, Degussa), 0.4 g of Sb-doped SnO_2 (Zelec ECP 3010-XC, Milliken chemicals) and 3 g of 3-methoxypropionitrile (3-MePRN) were ground vigorously in a mortar for 20 min. Then 9 g of MePRN and the gelator, 0.2 g of poly(vinylidenefluoride-co-hexafluoropropylene) (PVdF-HFP), was added to the mixture. The mixture was heated at 130 °C for 16 h to gelatinize it. As the commonly used carbon powder solvents such as water and ethanol boil below the melting point of PVdF-HFP [8, 9], 3-methothoxypropionitrile (3-MePRN) was used as a solvent in the carbon gel. Both 3-MePRN and PVdF-HFP have been used in the electrolyte of highly stable DSC [2, 3, 11], which is an excellent feature as their presence in the cell does not compromise the long term stability.

The carbon gel paste was deposited on ITO-PEN (15 Ω/sq, Peccell) by doctor blading using Scotch M3 removable tape as the frame. Each layer was heated at 110 °C for 5 min and then pressed (pressure 1000 kg/cm^2). 3 layers were made on each counter electrode resulting in thickness 7-10 μm which was measured with Dektak M6 Stylus Profiler.

The reference platinized counter electrodes were deposited on fluorine-doped tin oxide (FTO) coated glass (sheet resistance 15 Ω/sq, Hartford Glass Company, Inc.) with thermal platinization [6] at 385 °C for 15 min using 10 mM tetrachloroplatinate $PtCl_4$ (Sigma-Aldrich) dissolved in 2-propanol.

The photoelectrodes were made on FTO-glass with screen printing from titania paste (DSL 18NR-T, Dyesol). The TiO_2 films were sintered at 450 °C for 30 minutes. The resulting TiO_2 film thickness was ~14 μm. The layer was then sensitized in a dye solution consisting of 0.32 mM *cis*-bis(isothiocyanato)bis(2,2'-bipyridyl-4,4'-dicarboxylato)-ruthenium(II) bis-tetrabutylammonium (N-719, Dyesol) in ethanol (99.5 wt-%). 40 μm thick Surlyn ionomer resin film spacer (1601, DuPont) was used as frame foil and for the sealing. The cells were filled with a commercial liquid electrolyte (HSE-EL, Dyesol).

Photovoltaic measurements were made using a solar simulator providing 1000 W/m^2 AM1.5G (1 sun) equivalent light intensity and a Keithley 2420 SourceMeter to measure the current density – voltage (*i*-*V*) curves. In the measurements, the cells were placed on a black platform and provided with black masks with a slightly larger aperture size. Electrochemical impedance spectroscopy (EIS) was made with Zahner Elektrik's IM6 Impedance Measurement unit. The EIS measurements were carried out under illumination (red LED, 640 nm) at open circuit. The studied frequency range

was 100 mHz-100 kHz with 10 mV amplitude. The surface morphology was examined with JEOL JSM-7500FA, which is an analytical field emission scanning electron microscope (SEM).

3. Results and discussion

3.1. Mechanical properties and manufacturability

The main question that was addressed with the carbon gel catalyst layer was improved flexibility and adhesion. Firstly, there was no flaking of the carbon gel layer which has been a problem with the previously used carbon paste layers [9]. As Figure 2 shows, the carbon gel catalyst films represented excellent flexibility; the carbon gel films could be rolled even to 3 mm bend radius without any visible cracking. Even an ITO layer on the PET substrate does not survive such extreme bending stress. This great flexibility of carbon gel films can be fully utilized for instance when using metal substrates at the counter electrode.

Furthermore, the repeatability of the gel carbon counter electrodes was very good. The preparation procedure was easy and quick making it well suitable for industrial roll-to-roll production.

The SEM images of the carbon gel layer indicate that the layer is formed of clusters of ~5 μm in diameter (Figure 3a). The individual particles in the clusters are around 50 nm in diameter (Figure 3b). The white parts of Figure 3 are non-conducting which in practice means that they are composed of the gelator polymer PVdF-HFP. The gelator appears to be quite evenly distributed in the film (Figure 3).

3.2. Photovoltaic performance

The photovoltaic performance of the DSC with the low temperature carbon gel counter electrode was quite close to that of the DSC with thermally platinized counter electrode as Figure 4 shows.

The efficiency of the former was 4.24 % and that of the latter 4.81 %. The smaller efficiency of the DSC with carbon gel counter electrode was caused by the lower fill factor *FF*: carbon gel 54 % and thermal Pt 61 %. The reasons for the differences in the *FF* values are discussed in detail with EIS in section 3.3.

Both DSC with carbon gel and thermal platinization had similar V_{OC} and i_{SC} (Figure 4). This is to be expected as the open-circuit voltage V_{OC} and short circuit current density i_{SC} mostly depend upon the photoelectrode. Similarity of those values implies good initial stability of the counter electrode, e.g. no apparent detachment of catalyst material which would contaminate photoelectrode and decrease its performance.

3.3. Electrochemical performance

To analyze the lower *FF* of the DSC with carbon gel, EIS measurements were made under illumination at open circuit (OC). The comparison of the counter electrode responses of the different cells is straightforward when using the same current in the measurements (at OC current is zero) [12-14]. Conveniently, the cells gave also similar voltage at OC which enables the quantitative comparison of photoelectrode response as well [12, 13].

As presented in Figure 5a, both carbon gel and thermal Pt based cells show two semicircles in the Nyquist plots and two corresponding peaks in Figure 5b. In the case of thermal Pt cells, the high frequency peak corresponds to the charge transfer at the counter electrode and the low frequency peak to the charge transfer at the photoelectrode [12-15]. Contrary to that in the case of porous carbon electrodes, the response of the charge transfer at the counter electrode is actually at low frequencies, around 1 Hz [9]. The photoelectrode response is at the same frequencies [12-15], which causes an overlap of these responses. In other words, the charge transfer resistance R_{ct} at the carbon gel counter electrode and the recombination resistance at the photoelectrode R_{PE} form

together the large low frequency semicircle (42 Ωcm^2) in Figure 5a. As R_{PE} in the thermal Pt DSC was 19 Ωcm^2 and both carbon gel and thermal Pt cells had similar photoelectrodes, it can be estimated that R_{ct} in the carbon gel cells was 23 Ωcm^2. In the DSC with thermal Pt, R_{ct} was 12 Ωcm^2.

The R_{ct} of these carbon gel layer was also higher compared to the low temperature carbon layers presented in the literature. In the carbon gel, the gelator is electrically in active which lowers the surface area per density unit resulting in smaller R_{ct} value for a film with a given thickness. This is in practice the tradeoff between being able to get good flexibility to use roll-to-roll mass production and electrical performance.

In the carbon gel cells, there is also a high frequency semicircle (6 Ωcm^2) (Figure 5a). As there is no such response in the Pt cells at so high frequencies (Figure 5a), the response is apparently also related to the carbon gel counter electrode. That resistance might be caused by the contact resistance between the carbon catalyst layer and ITO-PEN (c.f. resistance between ITO-PEN and TiO_2 which typically also appears at high frequencies [14, 16]), or alternatively, the carbon gel catalyst layer is formed of a few different materials causing some contact resistance between them.

Both the ITO-PEN and FTO-glass had similar sheet resistance (15 Ω/sq). As the cells with the carbon gel counter electrode had almost same series resistance as Pt counter electrode (Figure 5), this suggests that the carbon gel catalyst layer did not significantly contribute to the sheet resistance.

4. Conclusions

The focus of this study was to improve the roll-to-roll manufacturability of counter electrodes for dye solar cells by using carbon gel catalyst layer on plastic substrates at low temperatures. The carbon gel showed excellent flexibility and suitability to roll-to-roll mass production. The

improvement of these essential qualities did not compromise the performance of the cell: the efficiency was only ~10 % lower compared to the conventional glass based DSC with thermally platinized counter electrode. The difference in the performance according to electrochemical impedance analysis was related to the lesser catalytic activity of the carbon gel compared to that of the thermally platinized layer.

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Figures and captions

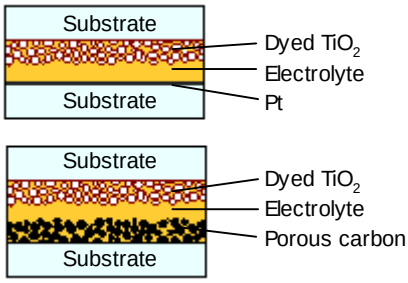

Figure 1. Structure of a DSC with Pt and porous carbon catalyst layers. Not in scale.

Figure 2. Bending of a counter electrode consisting of carbon gel catalyst layer on ITO-PET.

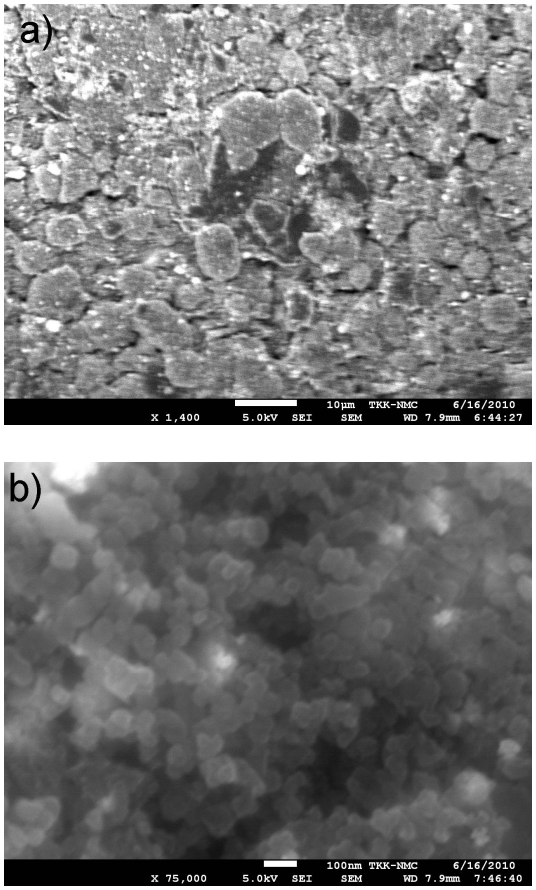

Figure 3. SEM images of the carbon gel layer. The scale indicated with the white bar is in a)10 µm and in b) 100 nm.

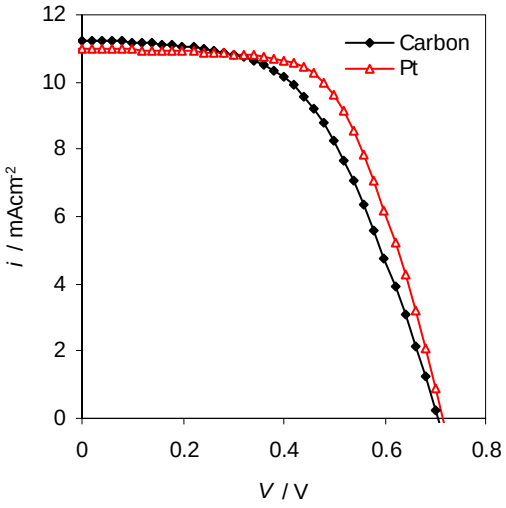

Figure 4. Typical *i*-*V* curves of the DSCs with carbon gel and thermally platinized counter electrode.

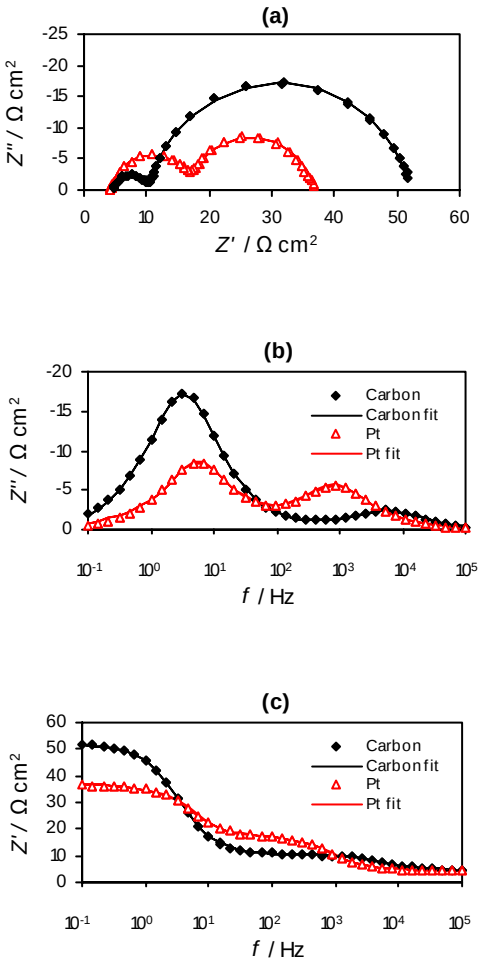

Figure 5. Typical measured (markers) and fitted (lines) EIS response of the DSCs with the carbon and Pt counter electrodes as a) Nyquist plot and b) imaginary impedance *Z''* and c) real impedance *Z'* as a function of frequency *f*. The marker and the line notations marked in b and c apply also for a.